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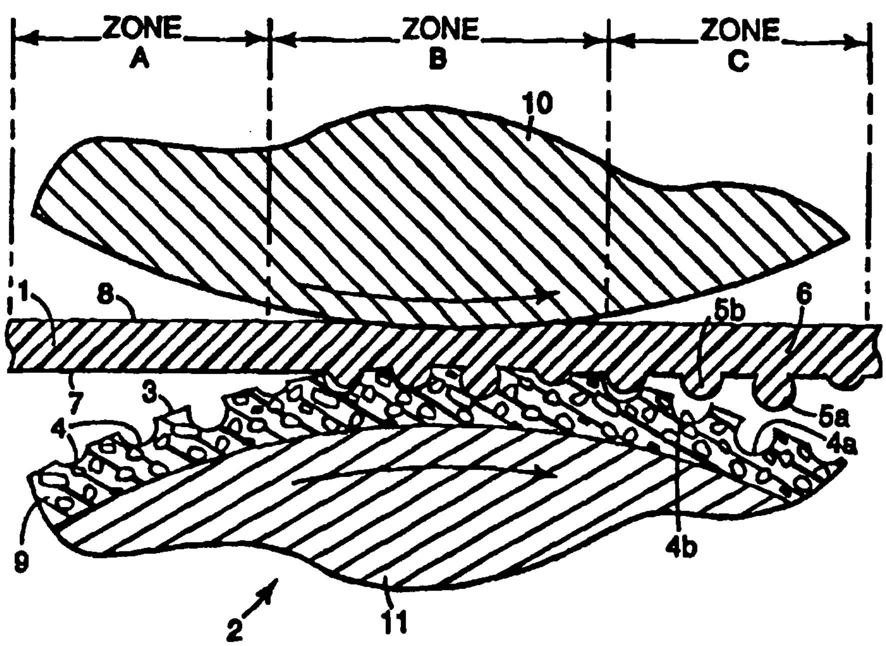

(57) Abstract

A method of preparing a polymeric substrate having a surface which includes a plurality of microaberrations (5a, 5b) is provided. A polymeric material (1) in a flowable state is contacted with a resilient surface (9) to form microaberrations (5a, 5b) which are inverted replicas of microaberrations (4a, 4b) present on the resilient surface. A cleaning article and a slip control material which include the microstructured polymeric substrate are also provided.

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MICROSTRUCTURED POLYMERIC SUBSTRATE

Background of the Invention

Polymeric substrates with a microstructured pattern on their surface have a wide variety of potential applications. Microstructured polymeric films may be applied to a surface in order to improve its slip control properties, e.g., to improve the grip on tools or athletic equipment. Other surfaces which may benefit from the application of materials providing enhanced slip control include traffic bearing surfaces, such as stairs, floors and ramps.

Polymeric substrates with a suitably textured surface may also be employed in cleaning articles. For example, non-abrasive polymeric scouring pads may be used for cleaning dishes or pots or for removing insects and other debris from windows. Polymeric materials have desirable physical properties for fabricating cleaning pads while offering the potential for very economical production costs.

A variety of methods for producing polymeric films having a textured surface are known. For example, an embossed thermoplastic film having a plurality of micro depressions imparted by placing a coarse sandblast pattern on a metal embossing roll is disclosed in U.S. Patent No. 5,229,186 (Tribble et al.). Similarly, U.S. Patent No. 4,861,635 (Carpenter et al.) describes the replication of negative images of microtopographical features from a metal chill roll or a Teflon™ covered metal roll onto a polypropylene film. U.S. Patent No. 4,463,045 (Ahr et al.) discloses the preparation of a plastic web having a microscopic pattern of surface aberrations by contacting a heated thermoplastic film with a photoetched metallic laminae which has a microscopic pattern of surface aberrations on the uppermost lamina.

The formation of a thermoplastic sheet having a plurality of "nubbles" is disclosed in U.S. Patent Nos. 4,239,286 (Louis et al.) and 4,327,730 (Sorenson). The nubbles are formed by contacting a ribbon of thermoplastic film with a texturing cylinder coated with a mixture of particles (e.g., aluminum oxide particles) and cured epoxy. An article with a microstructure-bearing surface is described in U.S. Patent No. 4,576,850 (Martens). The article is formed by filling a mold

master, which bears a microstructure, with a radiation curable oligomeric composition.

U.S. Patent Nos.4,772,444 (Curro et al.) and 5,221,276 (Battrell) disclose a microbubbled polymeric web. The microbubbles are produced by subjecting a flat polymeric film supported on a fine woven wire mesh to a high pressure liquid jet.

In order for the articles containing microstructured polymeric materials to realize their full potential, versatile, inexpensive methods of fabricating such polymeric materials must be available. Current methods do not readily allow controlled variations in the shape, orientation and positioning of a microscale texturing pattern on a polymer surface. In addition, current methodology typically only permits the generation of polymeric substrates in which the microstructure is limited to either the bottom of depressions or the tops of projections; it does not provide microstructure on the sides of macroscopic features such as depressions or projections nor does it permit a choice as to the type of microstructure generated.

A need, therefore, continues to exist for improved methods of producing polymeric substrates having a surface textured with a defined microscopic pattern. Optimally, such a method would also permit the introduction of macroscopic structural features (e.g., via embossing) and/or would allow the choice of generating a microscopic pattern on either all or a portion of the surface.

Summary of the Invention

The present invention provides a method of preparing a polymeric substrate having a surface which includes a plurality of microaberrations. The method includes contacting a flowable polymeric material with a resilient surface to form the microaberrations. The microaberrations produced on the polymeric surface are typically inverted replicas of microaberrations on the resilient surface, i.e., if the resilient surface includes a plurality of microdepressions, the polymer substrate which is generated will include a plurality of microprotrusions.

The present method also allows the formation of macroscopic features on the microstructured polymeric substrate. By incorporating embossing techniques, the present method permits the formation of polymeric substrates which include a

plurality of projecting elements having microaberrations on their outer surface. In particular, the method allows the formation of microaberrations on the side-walls of the projecting elements. If desired, the present method permits the introduction of microaberrations onto the entire surface of the polymeric substrate, i.e., on the portions of the surface in between the projecting elements (the "land area") as well as on the projecting elements themselves. The method also allows microaberrations to be generated only on the outer surface of the projecting elements and not on the land area.

In addition, the present method allows the production of a microstructured polymeric substrate having microaberrations with a variety of controlled shapes and sizes. The method may be employed with a wide range of polymeric materials capable of existing in a state which is sufficiently flowable to allow the polymer to conform to the resilient surface and are capable of being at least partially solidified under the processing conditions. The present method allows the economical production of a wide variety of polymeric articles having a microstructured surface which may optionally be simultaneously embossed to introduce macroscopic features.

The present method also provides a polymeric substrate having a plurality of projecting elements. The outer surface of the projecting elements has sidewalls which include a plurality of microprotrusions. The microprotrusions typically have a width and heighth of about 10μm to about 400μm.

In another embodiment, the present method provides a unitary polymeric substrate which includes a plurality of undercut-shaped solid microprotrusions. The polymeric substrate may also include a plurality of projecting elements having the microprotrusions on their outer surface.

Yet another embodiment of the present invention is directed to a dual structured polymeric substrate which includes a plurality of projecting elements. The outer surfaces of the projecting elements have sidewalls which include a plurality of microaberrations.

The present invention is also directed to cleaning articles and slip control materials which include the microstructured polymeric substrate. The

microstructured polymeric substrate may be formed by a process which includes contacting a flowable polymeric material with a resilient surface which has a plurality of first microaberrations. A microstructured polymeric substrate formed in this manner includes a plurality of second microaberrations which are inverted replicas of the first microaberrations.

Brief Description of the Drawings

Fig. 1 depicts a simplified schematic illustration of one embodiment of a method for producing a microstructured polymeric film according to the present invention.

Fig. 2 depicts a simplified schematic illustration of another embodiment of a method for producing a microstructured polymeric film according to the present invention.

Fig. 3 depicts a simplified schematic illustration of a third embodiment of a method for producing a microstructured polymeric film according to the present invention.

Fig. 4 depicts a simplified schematic illustration of a fourth embodiment of a method for producing a microstructured polymeric film according to the present invention.

Fig. 5 depicts a cross sectional view of a portion of a polymeric substrate of the present invention.

Fig. 6 shows an electron micrograph (12 X magnification) of a surface of a polymeric substrate of the present invention.

Fig. 7 shows an electron micrograph of one projecting element from the polymeric substrate depicted in Fig. 6 shown at a higher magnification (60 X magnification).

Fig. 8 shows an electron micrograph (15 X magnification) of a surface of a polymeric substrate of the present invention. The surface includes a plurality of projecting elements overlayed with a secondary structure of a plurality of raised ribs.

Fig. 9 shows an electron micrograph (50 X magnification) of a projecting element from a polymeric substrate of the present invention. The outer surface of the projecting element includes a plurality of cube corner out-shaped microprotrusions.

Fig. 10 shows an electron micrograph (50 X magnification) of a projecting element from a polymeric substrate of the present invention. The outer surface of the projecting element includes a plurality of cube corner in-shaped microdepressions.

Fig. 11 shows an electron micrograph (95 X magnification) of a projecting element from a polymeric substrate of the present invention. The outer surface of the projecting element includes a plurality of partially spherical microdepressions.

Fig. 12 shows an electron micrograph (60 X magnification) of a projecting element from a polymeric substrate of the present invention. The outer surface of the projecting element includes a plurality of undercut-shaped microprotrusions.

Fig. 13 shows an electron micrograph (18 X magnification) of a projecting element from a polymeric substrate of the present invention. The outer surface of the projecting element includes a plurality of microprotrusions.

Fig. 14 shows an electron micrograph (13 X magnification) of a surface of a polymeric substrate of the present invention. The surface includes a plurality of discontinuous projecting elements in the form ridges including a plurality of undercut-shaped microprotrusions. The substrate surface also includes a plurality of microprotrusions.

Fig. 15 shows an electron micrograph (13 X magnification) of a surface of a polymeric substrate of the present invention. The surface includes a plurality of undercut-shaped microprotrusions.

Fig. 16 depicts a cross sectional view of a portion of a master used to prepare a microstructured polymeric substrate of the present invention.

Detailed Description of the Invention

Fig. 1 depicts a schematic illustration of one embodiment of the present invention. A polymeric material 1 in a flowable state is brought into contact with a

resilient surface, such as the circumferential surface of resilient roll **2**. Resilient roll **2** includes an outer layer of resilient material **9** covering a cylindrical core **11**. The core **11** is typically formed from a substantially non-resilient material, such as a metal or a high durometer rubber. In zone A, the polymeric material is in a flowable state and has relatively smooth major surfaces **7** and **8**. The polymeric material may enter zone A already in flowable state, e.g., after exiting the die of an extruder. Alternatively, the polymer may be treated in zone A, such as by the application of heat, to transform the polymer into a flowable state. During processing, the flowable polymeric material comes into contact with the surface **3** of resilient roll **2** in zone B. Sufficient pressure is exerted in the nip on the flowable material by smooth roll **10** and resilient roll **2** to force the polymeric material to conform to the contours of surface **3**. The flowable polymer is forced into any recesses or crevices defined by the microdepressions **4** present in surface **3**. This results in the generation of microscopic projections **5a, 5b** ("microprotrusions") on the polymeric surface **7** which comes into contact with resilient surface **3**. The microprotrusions **5a, 5b** formed on the polymeric surface **7** are inverted replicas of the corresponding microdepressions **4a, 4b** in resilient surface **3**. While still in contact with the resilient surface **3**, the polymeric material solidifies to a sufficient degree to allow the microprotrusions **5a, 5b** to retain their shape (see zone C) as the microstructured polymeric film **6** is pulled away from the surface **3** and the microprotrusions **5a, 5b** are pulled out of microdepressions **4a, 4b**. This may be accomplished, for example, where the polymeric material is formed from a thermoplastic polymer by maintaining the temperature of the resilient roll **2** below the softening point of the polymeric material. Alternatively, where the polymeric material has thermoset properties, the solidification may be achieved by applying additional heat to the polymeric material while the material is in zone B, e.g., by maintaining smooth roll **10** at an elevated temperature.

The material which forms the surface **3** of resilient roll **2** typically permits the microstructured film **6** to be separated from resilient roll **2** without substantially distorting or destroying the microaberrations **5**. This requires that the forming microstructured film **6** does not adhere to resilient surface **3**. The outer surface of

resilient roll 2 may also be formed from a number of resilient materials which permit the processed polymer to be removed without problems of adhesion. In a preferred embodiment of the invention, resilient surface 3 is formed from a silicone rubber. Resilient materials formed from polyurethane or silicone permit the present method to be carried out under a wide range of processing conditions, e.g., temperatures from about 0°C to about 400°C or even higher.

The interaction between microaberrations 5, which are at least partially solidified, and the resilient roll surface 3 is such that the microaberrations 5 substantially retain their shape as the microstructured polymeric film 6 is pulled away from the resilient roll 2. To some extent this may be due to some resiliency on the part of the microaberrations 5 themselves, as where the solidifying polymeric material exhibits some degree of elasticity. More typically, the resilient interaction is achieved by the resiliency of the resilient roll surface material 9.

The resilient roll 2 may be covered with an outer layer of a porous resilient material, such as a polymeric foam. Examples of suitable foams for the resilient surface include polyurethane foams and silicone foams. The foam may be a closed cell polyurethane foam such as LS1525 polyurethane foam (available from EAR™ Specialty Composites Corporation, Indianapolis, IN) or PORON™ polyurethane foam (available from Rogers Corporation, East Woodstock, CT). The closed cell polyurethane foams disclosed in U.S. Patents 3,772,224 and 3,849,156, may also be employed for the resilient surface. Another example of a suitable polymeric foam is a closed cell silicone foam such as Bisco BF-1000 foam (available from Bisco Products, Elk Grove, IL). The resilient polymeric material may also include an open cell polymeric foam. Alternatively, the resilient surface may be covered with a layer of a nonporous flexible material, e.g., a flexible polymeric material such as a silicone rubber. For example, the resilient surface may include Silastic™ brand J-RTV silicone rubber (commercially available from Dow Corning Corp., Midland, MI). Resilient surfaces having defined microstructural features preferably include a silicone rubber. Alternatively, where the resilient surface has a foam microstructure, the resilient material preferably includes a closed cell polyurethane foam, such as described in U.S. Patents 3,772,224 and 3,849,156.

The resilient material which forms resilient surface **3** may inherently include microaberrations **4**, e.g., the pocket-like depressions present in the surface of a polymeric foam. Where the resilient surface includes a polymeric foam material, the resilient surface may also include a thin outer layer of a nonporous flexible material covering the foam. For example, the resilient surface may include a foam layer covered by a thin layer (e.g., about 0.5 mm to about 1.0 mm) of silicone rubber. The thin silicone rubber layer may include microaberrations on its surface.

The resilient surface may also be formed by wrapping the roll with a nonporous flexible microstructured material. For example, a variety of substantially rigid microstructured surfaces may be coated with a thin layer of material (e.g., liquid silicone rubber) which is then cured into a flexible material reflecting the microstructure of the underlying rigid structure. A desired pattern and shape of microprotrusions in a flexible material may also be generated by embedding a plurality of microscopic particles in the surface of a resilient material, such as by embedding inorganic particles (e.g., glass beads) in a silicone rubber layer. Microdepressions may be formed in silicone rubber layer (or other nonporous flexible material) by removing microparticles embedded in the silicone rubber to leave a plurality of microdepressions in the rubber surface.

A wide variety of polymers may be processed according to the present method into a polymeric substrate having a microstructured surface. Polymeric materials capable of being sufficiently flowable to allow the polymer to conform to the microscopic features of the resilient surface and capable of being solidified sufficiently to generate microscopic features on the polymer surface are suitable for use in the present invention. Typically, the polymeric material includes a thermoplastic polymer such as a polyolefin, although other polymeric materials capable of being processed in a flowable state, such as a B-staged thermoset polymer or a plastisol, may also be employed.

Typically, the polymeric material includes a thermoplastic polymer having a melt temperature above about 50°C. However, polymeric materials which exist in a flowable state at a considerably higher temperature may also be employed. The physical properties of the resilient surface and the polymeric material must be

matched such that the microstructural features of the resilient surface are stable and resilient under conditions which permit the flowable polymer to conform to the resilient surface and then at least partially solidify. Preferably, thermoplastic materials which can be passed through an embossing nip at or slightly above their glass transition temperature are employed, as such materials may be processed with short cycle times.

Examples of suitable thermoplastic polymeric materials which may be employed in the present process include polyolefins such as polypropylene, polyethylene, and polypropylene/polyethylene copolymers. Blends of polypropylene and/or polyethylene, such as a high/low molecular weight polyethylene blend (e.g., Hostalloy™ 731; Hoechst Celanese, Somerville, N.J.), are also suitable for use in the present invention. Other suitable thermoplastic polymers include polyvinyl chloride (PVC), polyamides such as a nylon (e.g., nylon 6, nylon 6,6, or nylon 6,9), and polyesters. Olefin copolymers such as ethylene/vinyl acetate copolymers or copolymers of an olefin and an a,b-unsaturated acid (e.g., an ethylene/methacrylic acid copolymer reacted with metal salts to confer ionic character; available from E.I. du Pont de Nemours & Co., Inc. as Surlyn™ 8527) may also be employed in the present invention. Preferably, the polymeric material includes a polyolefin.

In another embodiment of the invention, the polymeric material may include a plastisol. The plastisol includes a dispersion of thermoplastic resin particles (e.g., polyvinyl chloride resin particles) in a plasticizer and may also include a volatile organic solvent. Examples of suitable plastisols which may be used in the present method include the vinyl plastisols such as #D1902-50 Black and #D1902-78 White available from Plast-O-Meric, Inc. (Waukesha, WI).

The microaberrations generated on the polymeric substrate by the present method may have a wide variety of shapes and orientations. The microaberrations include microprotrusions and/or microdepressions. These may be in a random and/or ordered pattern. The microaberrations may include irregular shapes and/or regular geometric shapes, e.g., a plurality of discrete mounds, posts, cones, truncated cones, pyramids, or truncated pyramids. The microaberrations may include discontinuous shapes, i.e., a plurality of discrete projections or depressions.

Alternatively, the microaberrations may include continuous forms such as ridges and grooves. The dimensions of the microaberrations, however, are typically small enough to leave the form of any macroscopic features on the polymeric substrate substantially unaltered. Typically, discontinuous microaberrations have a maximum dimension (height or width) of no more than about 400μm. Preferably, discontinuous microaberrations have a maximum height of no more than about 300μm and a maximum width of no more than about 300μm. More preferably, discontinuous microaberrations have a maximum height of no more than about 200μm and a maximum width of no more than about 200μm. Similarly, where the microaberrations are continuous in nature, the height and width of the microaberrations are typically no more than about 400μm, preferably of no more than about 300μm, and more preferably of no more than about 200μm. The microaberrations preferably have an average minimum height and width of at least about 10μm and more preferably at least about 25μm.

One distinct advantage of the present method is that it allows the generation of undercut-shaped microaberrations on the surface of a polymeric substrate. As used herein, the term "undercut-shaped" is defined as a shape having a cross-sectional surface area which increases and then typically decreases along a perpendicular vector away from the polymer surface. In other words, the cross-sectional surface area is measured in a plane parrallel to the major surface of the polymeric substrate with respect to which the undercut-shaped microaberration in question is positioned.

The microstructured polymeric film **6** formed by the process illustrated in Fig. 1 includes a number of undercut-shaped microprotrusions **5a**. The undercut-shaped microprotrusions are generated when the flowable polymeric material is forced into an undercut-shaped microdepression **4a** in resilient surface **3**. The parameters of the process (e.g., temperature of the thermoplastic polymeric material in Zone A, temperature of the resilient surface **3**, the compositions of the polymeric material and resilient surface **3**, the speed at which the polymeric film is processed and pressure exerted on the forming microstructured polymeric film) may be adjusted such that an undercut-shaped microprotrusion **5a** on the polymeric film

may be pulled out of an undercut-shaped microdepression **4a** without substantially altering or distorting the shape of the microprotrusion.

In addition to facilitating the generation of a microstructured surface on a polymeric substrate, the use of a resilient surface having an outer resilient layer of foam or silicone rubber has another advantage. The polymeric substrate may also be simultaneously shaped or formed to introduce macroscopic features, e.g., by embossing, as part of the present method. Figure 2 shows a second embodiment of the present method. The resilience of outer layer **32** of chill roll **27** permits the film to be embossed without requiring that each projecting embossing element **21** be precisely positioned with respect to a corresponding recess in the opposing roll.

In the embodiment of the present method illustrated in Fig. 2, a flowable polymeric material **25**, such as a softened thermoplastic polymeric film, is passed through a nip which includes embossing roll **20** and chill roll **27**. Chill roll **27** is covered by a outer layer **32** of resilient material which has a plurality of microdepressions **28** in its outer surface **30** (e.g., the microdepressions present in the surface of a polymeric foam). When the softened thermoplastic polymeric film **25** is contacted with embossing roll **20** and chill roll **27**, posts **21** are forced into the film and projecting elements **22** are formed. As this happens, the softened thermoplastic polymeric film **25** is forced into intimate contact with the surface **30** of chill roll **27**. As with the method illustrated by Fig. 1, this results in the formation of microprotrusions **23** on the portions of the polymeric material in contact with surface **30**. The microprotrusions **23** are inverted replicas of the corresponding microdepressions **28** in the outer surface **30** of chill roll **27**. The resulting polymeric film **26** has a plurality of projecting elements **22** having a hollow core **29**. The outer surface **24** of projecting elements **22** includes a plurality of the microprotrusions **23**. In the process illustrated in Fig. 2, the microprotrusions **23** are generated on the top **24** and side **33** surfaces of projecting elements **22**, but not on the land area **31** between adjacent projecting elements **22**.

By controlling the nip pressure, the present process may be modified to produce microaberrations on either the outer surface of the projecting elements **22** or on the entire surface of the polymeric film (i.e., on the land area **31** between the

projecting elements 22 as well as on the outer surfaces 24, 33). The nip pressure may be increased by a variety of techniques, including but not limited to positioning embossing roll 20 and chill roll 27 closer together, increasing the height of embossing elements 21 or decreasing the density of embossing elements 21 (i.e., increasing the spacing between adjacent embossing elements 21 and decreasing the surface area of embossing roll 20).

Fig. 3 illustrates a third embodiment of the present method. Softened thermoplastic polymeric film 46 is passed through a nip which includes embossing roll 40 and chill roll 41. Chill roll 41 is covered with two layers of resilient material, an inner layer of polymeric foam 43 and an outer layer 44 of nonporous flexible material, such as silicone rubber. The surface 47 of layer 44 has a microstructure which includes a plurality of microprotrusions 45. The nip pressure forces the softened polymeric film 46 into contact with embossing roll 40 and chill roll 41. As this occurs, posts 42 are pressed into the film 46 to form projecting elements 48. During this process, the softened film 46 is forced into intimate contact with the microstructured surface 47 of chill roll 41. As with the methods illustrated by Figs. 1 and 2, microscopic features (microdepressions 49) are generated in the portions of the film 46 in contact with surface 47.

The microstructured polymeric film 50 produced by the method illustrated in Fig. 3 has a plurality of projecting elements 48 having a hollow core 51. The projecting elements 48 include a plurality of the microdepressions 49, which are inverted replicas of corresponding microprotrusions 45 in the outer surface 47 of chill roll 41. In the process illustrated in Fig. 3, the microdepressions 49 are generated on the land area 53 as well as on the top 52 and sidewall 54 surfaces of projecting elements 48. By controlling the nip pressure, it is also possible to cause the microscopic features to be generated only on the outer surfaces of the projecting elements (as illustrated in Fig.2).

The microprotrusions 45 depicted in Fig. 3 may be formed from a flexible material, such as silicone rubber. The present method may also be carried out with a resilient surface which includes a plurality of nondeforming microscopic regions surrounded by resilient material, e.g., a plurality of rigid microscopic particles

partially embedded in the surface of a resilient material. For example, the resilient surface may be formed from a layer of silicone rubber which has a plurality of microscopic inorganic particles (e.g., glass beads having a diameter of about 10μm to about 250μm) partially embedded in surface of the rubber layer. Because of the flexibility of the underlying silicone rubber matrix, it is possible to generate microdepressions in the surface of a polymeric substrate which are substantially undistorted inverted replicas of the shape of the inorganic particles protruding from the silicone rubber surface. In other words, if the inorganic particles are spherical microscopic glass beads which partially protrude from the silicone rubber, a plurality of microdepressions, which are shaped like a portion of a sphere, may be formed in the polymer substrate surface. In addition, due to the flexibility of the resilient surface, the present method permits the generation of embossed polymeric substrates having microdepressions and/or microprotrusions on the sidewalls of macroscopic structural features formed via embossing.

Fig. 5 depicts a portion of a polymeric film **80** which has been embossed according to the present method to generate a hollow projecting element **82**. The projecting element **82** includes microdepressions on both its top outer surface **83** and its outer sidewalls **84**. By employing the present method, it is possible to create microdepressions on the sidewalls of a projecting element such that the microdepressions are substantially undistorted inverted replicas of rigid microprotrusions on the resilient surface used to form the microstructured embossed polymeric substrate. Microdepressions having a partially spherical shape (see, e.g., microdepressions **81** in Fig. 5) may be formed by employing a resilient surface which includes rigid partially spherical shaped microprotrusions, such as glass beads partially embedded in a resilient material.

Fig. 4 illustrates yet another embodiment of the present method. Resilient roll **60** includes an outer layer of resilient silicone rubber material **70**. The surface **62** of the resilient material **70** includes a number of macroscopic depressions **63**. In addition, the entire resilient surface **62** includes a plurality of microdepressions **64**. As the flowable polymeric material **69** is passed through the nip of resilient roll **60** and smooth roll **61**, surface **68** of polymeric material **69** is forced into intimate

contact with resilient surface **62**. This causes the polymeric material to fill macroscopic depressions **63**, thereby generating solid projecting elements **65** extending from dual structured film **67**. In the process illustrated in Fig. 4, the polymeric material is simultaneously forced into microdepressions **64**, thereby generating a plurality of solid microprotrusions **66** on the entire surface of textured polymeric substrate **67** (i.e., on the land **72** as well as on the outer surface **71** of projecting elements **65**).

The projecting elements formed by the present method may have a variety of heights. For example, the method allows the production of microstructured projecting elements having a height within the range of about 0.375mm to about 2.5mm while avoiding substantial distortion of microaberrations generated on the outer sidewalls of the projecting elements. Moreover, the present method allows undistorted microaberrations to be formed in the sidewalls of projecting elements which have a very steep draft. For example, substantially undistorted microaberrations may be formed on the sidewalls of projecting elements having a draft of less than about 30° (with respect to a vector perpendicular to the major surface of the polymeric substrate). Substantially undistorted microaberrations may be generated on sidewalls which are quite close to being vertical (i.e., have a draft of less than about 10°) or even on sidewalls which are substantially vertical (i.e., have a draft of less than about 5°). Using the present method, substantially undistorted microprotrusions have been generated on the sidewalls of vertical (i.e., 0° draft) 1.5mm high hollow posts. This unitary polymeric structure was generated by embossing a polypropylene film into a resilient roll covered with a layer of a closed cell polyurethane foam.

The microstructured polymeric substrates of the present invention may be used to form a slip control material. For example, a unitary polymeric sheet having microaberrations on one face may be afixed to traffic bearing surfaces, such as stairs, floors and ramps. Polymeric materials formed by the present method may also used to form the grip on tools or athletic equipment thereby providing enhanced slip control.

In yet another embodiment of the invention, the microstructured polymeric substrates of the present invention may be used to form a cleaning article. In particular, flexible polymeric sheets which have been embossed to form a unitary polymeric structure having a plurality of microtextured projecting elements are useful in cleaning applications. Such a flexible sheet of polymeric material may be textured using the present method. Flexible sheets of this type may be utilized as a cleaning rag or may be afixed to a foam backing to form a cleaning pad.

The invention is further characterized by the following examples. These examples are not meant to limit the scope of the invention as described in the foregoing description. Variations within the concepts of the invention will be apparent to those skilled in the art.

Process Parameters

Embossed polypropylene films were prepared by extruding polypropylene resin (DS7C50, available from Shell Chemical Co., Houston, TX) from a single screw extruder (Model DS15H, available from Davis Standard, Stamford, CT) equipped with a 3.8 cm diameter cylinder, into the nip of a two roll embossing apparatus. The extruder, which was operated at 254°C, delivered a 22.9 cm wide sheet of molten polypropylene through a 30.5 cm die having a 0.25 mm die gap at a rate of 55 g/m^2, vertically downward into the nip of the embossing apparatus which was positioned about 7.6 cm below the die. The embossing apparatus utilized two 24.5 cm diameter by 30.5 cm long steel rolls having independent temperature controls. One of the rolls (the embossing roll) was heated to 49°C and carried an embossing pattern while the other roll (the chill roll) was cooled to 7°C and was covered with a resilient material. The polypropylene was embossed at a nip pressure of 138 kPa and line speed of 1.5 m/min.

<u>Embossing Apparatus/Process II</u>

An embossed polyethylene film was prepared by extruding polyethylene (DOWEX™ 2047A, available from Dow Chemical Co., Midland, MI) from a single screw extruder (Model 1.75 TMC30; HPM Corporation, Mount Gilead, OH)

equipped with a 4.4 cm diameter cylinder into the nip of a two roll embossing apparatus. The extruder, which was operated at 249°C and a screw rotational speed of 20 rpm, delivered a sheet of molten polyethylene through a 30.5 cm die having a 0.25 mm die gap horizontally into the nip of a two roll embossing apparatus which was positioned such that the width of the polyethylene film entering the nip was approximately 15 cm. The embossing apparatus utilized a 25.4 cm diameter by 35.6 cm long steel roll (the embossing roll) which carried an embossing pattern and a similarly sized 75 durometer rubber roll which served as the chill roll. The steel roll was heated to 15.6°C, while the rubber roll, which was covered with a resilient material, was cooled to 0°C. The polyethylene was embossed at a nip pressure of 55 kPa and line speed of 3 m/min.

<u>Embossing Roll Surfaces</u>

The embossing roll surfaces were generated by conventional photoengraving techniques on magnesium or a magnesium alloy. Specific embossing patterns used in the following examples included:

EB-1

A hexagonal close packed array of circular posts (1.0 mm in diameter, 0.5 mm in height) which were spaced 1.9 mm on center.

EB-2

A square lattice array of square posts (1.0 mm on a side, 1.0 mm in height) which were spaced 2.5 mm on center.

EB-3

A square lattice array of circular posts (1.0 mm in diameter, 1.0 mm in height) which were spaced 1.9 mm on center.

EB-4

A herringbone pattern consisting of discontinuous ridges 1.5 mm in height and having top rectangular surfaces 1.0 mm in length and 0.13 mm in width. The rectangular base dimensions of the discontinuous ridges were larger than the top surface dimensions as the sidewall portions were inclined at an approximately 25-30° angle to a vector

perpendicular to the face of the embossing roll. The center-to-center spacing of the ridges was 4.4 mm in the down web direction and 3.5 mm in the cross web direction. The ridges were positioned at a 30° angle to the left or right of the down web direction, i.e., the rows of discontinuous ridges alternated between 30° left and right of the down web direction.

Chill Roll Covers

Chill rolls were covered with one or more layers of foam, a resilient patterned silicone rubber sheet or a laminate construction of a foam and a resilient patterned silicone rubber sheet. Specific foam materials that were used in the following examples included:

RC-1

A 3.2 mm thick layer of polyurethane foam prepared as generally described in U.S. Pat. Nos. 3,772,224 (Marlin et. al.) and 3,849,156 (Marlin et. al). The foam was prepared from a four part mix (A-D), the composition of which were:

Part A - 100 parts of a polyol mixture of consisting of Niax 24-32 (97.77 parts) and Niax E-434 (2.23 parts), polyether polyols (available from Arco Chemical Co., Newton Square, PA) dipropylene glycol (9.18 parts per hundred parts polyol (php); fragrance grade), Niax LC-5615 (3.74 php, a nickel catalyst composition available from OSI Specialities, Lisle IL), aluminum trihydrate filler (54.59 php, Aloca C-331, available from Aluminum Company of America, Bauxite, AR), and Hostaflam AP 442 flame retardant (16.38 php, available from Hoechst Celanese Corp., Charlotte, NC);

Part B - 37.39 php of an isocyanate mixture consisting of 4,4'-diphenylmethane diisocyanate and a modified 4,4'-diphenylmethane diisocyanate (Rubinate 1920 available from ICI, Rubicon Chemicals, Geismer, LA);

Part C - 4.77 php of a 70.9% (w/w) solution of a silicone surfactant (L-5614, available from OSI Specialities) in a polyether glycol (Niax E-351, available from Arco Chemical Co.); and

Part D - 6.71 php of an approximately 8% solids (w/w) dispersion of carbon black (Product No. 1607029, available from Spectrum Colors, Minneapolis, MN) in polyether glycol (Niax E-351).

Separate feed streams of the four parts were pumped into a 90 mm dual head Oakes Frother (available from ET Oakes Corp., Hauppauge, NY) through an entrance manifold attached to the frother. The mixture was frothed by injecting high purity nitrogen through a capillary tube located at the entrance to the frother. The frothed mixture was processed through the frother at a mixing speed of 800 rpm and a discharge pressure of about 0.55 MPa and dispensed from an approximately 2.6 m x 1.3 cm hose onto a polyester film and spread over the film using a knife coater (2.4 mm gap). The foam was cured by passage through a 3 chambered 13.7 m forced air oven at a line speed of 1.5-1.8 m/minute. The first chamber was maintained at 135°C. The second and third chambers were maintained at 154°C.

RC-2

A 6.3 mm thick layer closed cell silicone foam (Bisco BF-1000, available from Bisco Products, Elk Grove, IL).

Patterned silicone rubber sheets used alone or in silicone rubber sheet/foam laminate chill roll cover constructions were prepared by applying an approximately 0.8 mm thick coating of uncured silicone rubber (Silastic™ brand J-RTV silicone rubber, available from Dow Corning Corporation, Midland, MI) over a structured surface, curing the silicone rubber at 66°C for one hour, and removing the cured patterned silicone rubber sheet to provide a resilient replica of the structured surface. Specific silicone rubber sheet patterns and silicone rubber sheet/foam laminate constructions used in the following examples included:

RC-3

A silicone rubber sheet having a pattern of parallel raised ribs 0.18 mm in height and spaced 0.36 mm apart, the sides of which intersect at a 90° angle, which was replicated from the surface of Optical Lighting Film (3M, St. Paul, MN). This silicone rubber sheet was laminated to a layer of the closed cell polyurethane foam **RC-1**, described above, to form a chill roll cover material.

RC-4

A silicone rubber sheet having a pattern of cube corner recesses 0.18 mm in depth with a base triangle having angles of 55°, 55°, and 70°, replicated from the surface of a cube corner reflective polycarbonate film as described in U.S. Pat. No. 4,588,258 (Hoopman).

RC-5

A silicone rubber sheet having a pattern of cube corner protrusions 0.09 mm in height arrayed in a pattern similar to that of **RC-4**.

RC-6

A silicone rubber sheet having a random pattern of spherical projections (ranging from approximately 10-25% of a total sphere). The silicone rubber sheet was prepared by (1) randomly capturing glass beads, about 55 mm in diameter, in a 5 mm (dry thickness) adhesive (F-10, an acrylic base adhesive containing a solvent vehicle, available from Rohm & Haas, Philadelphia, PA) coated on polyethylene coated Kraft paper; (2) coating silicone rubber (Silastic™ brand J-RTV silicone rubber) over the glass beads using a knife coater with a coating gap of 0.5 mm; (3) placing the uncured coating in a partial vacuum to remove entrapped air; (5) curing the degassed coating at 70°C for two hours, and (6) removing the cured silicone rubber from the adhesive coated Kraft paper.

RC-7

A silicone rubber sheet having a random pattern of spherical depressions (ranging from approximately 75-90% of a total sphere)

prepared by removing the glass beads from roll cover **RC-6**. The glass beads were removed by applying Scotch™ 810 Magic™ Mending Tape (available from 3M, St. Paul, MN) to the glass bead containing surface and flexing the silicone film as the adhesive tape was removed.

Example 1

An embossed polypropylene film was prepared using Embossing Apparatus/Process 1, incorporating an embossing roll having a hexagonal array of circular posts (**EB-1**) and a closed cell polyurethane foam chill roll cover (**RC-1**). Electron photomicrographs of the face of the embossed film that had been in contact with the chill roll cover (see Figs. 6 and 7) show projecting elements consisting of a hexagonal close packed array of hollow circular posts covered with microaberations consisting of a plurality of microprotrusions corresponding to inverted replicas of surface pores in the foam chill roll cover, many of which had an undercut structure. The microprotrusions, which covered the top and side surfaces of the posts, were not present on the land area or surface area between the projecting elements.

Example 2

An embossed polypropylene film was prepared according to the procedure of Example 1 except that the embossing roll had a square lattice array of square posts (**EB-2**) and the chill roll cover was a silicone rubber sheet having a ribbed pattern which was laminated to a layer of polyurethane foam (**RC-3**). An electron photomicrograph (see Fig. 8) of the face of the embossed polypropylene film, which had been in contact with the chill roll cover, shows projecting elements consisting of a square lattice array of hollow square posts. The surfaces of the square posts were covered with an array of protruding parallel ribs. The ribs were observed on the top and side surfaces of the posts as well as the land area between the posts.

This experiment demonstrates that in generating microaberations in a polymer film which are inverted replicas of microaberations on the surface of a

resilient chill roll, the shape of the microaberations need not be limited to pores in the surface of a foam.

Example 3

An embossed polypropylene film was prepared according to the procedure of Example 1 except that the embossing roll had a square lattice array of circular posts (**EB-3**) and the chill roll cover was a silicone rubber sheet having a cube corner recess pattern (**RC-4**). An electron photomicrograph (see Fig. 9) of the face of the embossed polypropylene film that had been in contact with the chill roll cover shows projecting elements consisting of a square lattice array of hollow circular posts. The top and side surfaces of the posts were covered with a pattern of protruding cube corners. The land area between the posts was smooth.

Example 4

An embossed polypropylene film was prepared according to the procedure of Example 2 except that the chill roll cover was a silicone rubber sheet having cube corner projections (**RC-5**). An electron photomicrograph (see Fig. 10) of the face of the embossed polypropylene film which had been in contact with the chill roll cover showed projecting elements consisting of a square lattice array of hollow square posts. The top and side surfaces of the posts were covered by an array of recessed cube corners ("microdepressions"). The land area between the posts was also covered the same array of cube corner microdepressions.

Example 5

A 5 cm square piece of flat tooling with a square lattice array of square posts (1.0 mm on a side, 1.0 mm in height) spaced 2.0 mm on center was heated to 193°C on a hot plate. A 0.26 mm thick piece of polypropylene (DS7C50) film was placed on the patterned side of the tooling and heated until the polypropylene film softened (approximately 1 minute). Once softened, the polypropylene film was covered with a silicone rubber sheet embedded with glass beads (**RC-6**) such that the bead containing surface contacted the softened polypropylene. Two layers of

the closed cell polyurethane foam chill roll cover (**RC-1**) were placed on top of the silicone rubber sheet, the assembly removed from the hot plate, and pressure applied to the assembly by means of a hand held platen until the polypropylene solidified. An electron photomicrograph of the face of the embossed polypropylene film that had been in contact with the silicone rubber sheet showed a square lattice array of projecting hollow square posts (see Fig. 11) covered with microaberations. The microaberations consisted of a random array of spherical microdepressions (ranging from approximately 10-25% of a total sphere). The microdepression pattern was observed on the top and side surfaces of the posts as well as the land area between the posts.

Example 6

An embossed polypropylene film was prepared according to the procedure of Example 5 except that the silicone rubber sheet had a random pattern of spherical microdepressions (**RC-7**). A number of the spherical microdepressions had an undercut shape. An electron photomicrograph of the face of the embossed polypropylene film that had been in contact with the silicone rubber sheet showed a unitary structure which included a square lattice array of projecting hollow square posts (see Fig. 12) covered with a pattern of microaberations. The microaberations consisted of a random array of spherically shaped polypropylene microprotrusions. The microprotrusion pattern was observed on the top and side surfaces of the posts as well as the land area between the posts. Since the polypropylene microprotrusions were inverted replicas of the microdepressions in the silicone rubber sheet, a number of the microprotrusions had a spherical undercut shape.

Example 7

An embossed polyethylene film was prepared using Embossing Apparatus/Process II, incorporating an embossing roll having a square lattice array of square posts (**EB-2**) and a closed cell silicone foam chill roll cover (**RC-2**). An electron photomicrograph (see Fig. 13) of the face of the embossed polyethylene that had been in contact with the chill roll cover shows a primary structure

consisting of a square lattice array of projecting hollow square posts covered with microaberations. The microaberations consisted of a random array of microprotrusions corresponding to inverted replicas of the surface pores in the foam chill roll cover. The microprotrusions were observed on the side surfaces as well as on the tops of the posts.

Example 8

An embossed film was prepared using a procedure similar to the procedure of Example 7. An ethylene/propylene copolymer (KS-057, available from Himont USA, Inc., Wilmington, DE) was substituted for the polyethylene resin. The embossing roll had a herringbone pattern of discontinuous ridges (**EB-4**). The chill roll was covered with a layer of a closed cell polyurethane foam (**RC-1**). The ethylene/polypropylene copolymer was processed at a nip pressure of 6.9 kPa and line speed of 1.5 m/min. The temperatures of the inlet fluids to the embossing roll and chill roll were 15.6°C and 0°C, respectively. An electron photomicrograph (see Fig. 14) of the face of the embossed film that had been in contact with the chill roll cover showed of a herringbone pattern of discontinuous ridges covered with a plurality of microprotrusions. The microprotrusions corresponded to inverted replicas of the surface pores in the foam chill roll cover.

Example 9

An embossed polypropylene film was prepared using Embossing Apparatus/Process I except that a smooth steel roll, which was maintained at 54°C, was substituted for the embossing roll. The extruder was operated at 266°C, and the polypropylene was delivered at a rate of 159 g/m^2. The chill roll was covered with a closed cell urethane foam (**RC-1**). An electron photomicrograph of a cross-section of the resulting unitary microstructured film (Fig. 15) showed a plurality of microprotrusions on the face of the embossed film which had been in contact with the chill roll. The microprotrusions corresponded to inverted replicas of the surface pores of the foam chill roll cover. Many of the microprotrusions showed an undercut-shaped structure.

Examples 10-13

A series of embossed films were prepared using Embossing Apparatus/Process I except that a variety of thermoplastic polymers were substituted for the polypropylene and embossing conditions were correspondingly changed to allow processing of the polymers. The polymers, processing conditions, and the roll covers used to prepared the embossed films are summarized in Table 1. All films were prepared using an embossing roll having a square lattice array of square posts (**EB-2**).

Table 1

Thermoplastic Polymer/Operating Conditions

Expl	Polymer	Chill Roll Cover	Extruder Operating Temp(°C)	Chill Roll Temp(°C)	Embossing Roll Temp(°C)	Line Speed (m/min)
10	Surlyn™ 8527	RC-1	225	7	54	1.5
11	Nylon 6,9[1]	RC-4	254	18	38	1.5
12	Hostalloy™ 731	RC-1	305	18	38	0.6
13	PVC[2]	RC-4	170	16	38	0.6

1. Vydyne™, available from Monsanto, St. Louis, MO.
2. Apex Telcar™, available from Teknor Apex Co., Pawtucket, RI.

In Examples 10 and 12, the face of the film in contact with the chill roll bore microaberations consisting of a plurality of microprotrusions corresponding to inverted replicas of the surface pores of the foam chill roll cover. In Examples 11 and 13, the face of the film in contact with the chill roll bore microaberations consisting of a pattern of protruding cube corners.

Example 14

A microstructured polymeric substrate was prepared by the following procedure.

One end of a piece of 3MÔ Optical Lighting Film #2300 Acrylic (available from 3M, St. Paul, MN), approximately 90 cm X 10 cm, was secured, grooved face down, to a bench top with masking tape. The 3MÔ Optical Lighting Film has a plurality of substantially 90° included angle ridges. The depressions in the surface of the film are about 0.18 mm in depth. The unsecured end of the film was grasped in a manner such that a tear could be initiated in a grove approximately 2 cm from the edge of the film and the film torn along its length. The film was torn at an angle of between approximately 15-30° from the horizontal to produce a clean, straight edge having a substantially constant acute angle along one piece of the film and a complementary obtuse angle on the edge of the adjacent piece of film. Strips produced in this manner were cut into approximately 6.5 cm lengths (herein after referred to as "master elements") and used to assemble a master **112**, a portion of the cross-section of which is illustrated in Fig. 16, in the following manner:

The grooved faces **105, 106** of two master elements were nested together so that the acute tear angle edge **100** of one element (B in Fig. 16) extended beyond the obtuse tear angle edge **101** of the second element (A in Fig. 16) by four ridges. The smooth face **102** of a third master element (C in Fig. 16) was then placed against the smooth face **103** of the second master element (B) with the acute tear angle edges **100, 104** aligned. The grooved face **108** of a fourth master element (D in Fig. 16) was then nested with the grooved face **107** of the third master element (C) such that the obtuse angle tear edge **109** was indexed four groves below the acute tear angle edge **104** of the third element (C) and aligned with the obtuse tear angle edge **101** of the first master element (A). The stacking pattern (ABCDABCD.....) was repeated until a master, approximately 1.2 cm X 6.5 cm was assembled. The total assembly was clamped together using a number of binder clips (5/8 inch capacity binder clip No. 100500 distributed by IDL Corp., Carlstadt, NJ).

A master mold of the master **112** was prepared according to the following steps:

a) Forcing a vinyl siloxane dental impression material (3M ExpressÔ, available from 3M, St. Paul, MN) into the contoured edge of the master with the manufacture's supplied application device, being careful to avoid entrainment of air bubbles between the impression material and the master;

b) Containing a pool of the dental impression material on a glass plate between two aluminum spacer bars (approximately 0.32 cm X 1.25 cm X 2 cm) positioned approximately 2.5 cm apart;

c) Centering the master over the spacer bars such that each end of the master overlapped each spacer bar approximately 0.5 cm and forcing the impression filled face of the master into the pool of impression material until the impression filled edge of the master contacted the spacer bars;

d) Positioning two additional aluminum bars (approximately 0.6 cm X 0.6 cm X 10 cm) in the impression material pool such that these bars contacted the ends of the spacer bars, thereby forming a containment well for the impression material;

e) Allowing the impression material to cure;

f) Removing the master from the cured impression material and trimming the ends of the cured mold to provide an approximately 2.5 cm long mold of the master; and

g) Securing end dams to the trimmed mold to provide a well for subsequent molding of polymeric materials in the mold.

Microstructured polymeric substrates were prepared by filing the master mold with a vinyl plastisol (#D1902-50 Black, available from Plast-O-Meric, Inc., Waukesha, WI) and curing the plastisol in a circulating air oven at 204°C (400°F) for 15 minutes. The cured plastisol was demolded to produce a flexible, compliant polymeric substrate (50 durometer) having a plurality of grooved ridges. The grooves ("microaberations") in the ridges were replicas of the grooves **111** in the sidewalls of the grooved ridges **110** of master **112** (and inverted replicas of the of the continuous protrusions on the sides of the depressions in the master mold).

Example 15

Microstructured polymeric substrates having a plurality of grooved ridges were prepared from the master mold of Example 14, substantially following the procedure of Example 14, except that a firmer vinyl plastisol (#D1902-78 White, available from Plast-O-Meric, Inc.) was used to form the polymeric substrates (78 durometer).

All publications and patent applications in this specification are indicative of the level of ordinary skill in the art to which this invention pertains.

The invention has been described with reference to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications may be made while remaining within the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1) A method of producing a polymeric substrate comprising:

contacting a polymeric material in a flowable state with a resilient surface and an embossing surface to produce a microstructured polymeric substrate;

the resilient surface comprising a plurality of first microaberrations and the embossing surface comprising a plurality of embossing elements projecting therefrom;

wherein the microstructured polymeric substrate comprises a plurality of hollow projecting elements comprising an outer surface, the outer surface comprising a plurality of second microaberrations which are inverted replicas of the first microaberrations.

2) The method of claim 1 wherein the polymeric material comprises a thermoplastic polymer which comprises a polyolefin, a polyamide, polyvinyl chloride, a polyester or an olefin copolymer.

3) The method of claim 1 wherein the resilient surface comprises a polymeric foam or a nonporous flexible polymeric material.

4) The method of claim 3 wherein the resilient surface comprises a nonporous flexible polymeric material comprising a plurality of rigid microparticles embedded therein.

5) A method of producing a polymeric substrate comprising:

contacting a polymeric material in a flowable state with a resilient surface to produce a microstructured polymeric substrate;

the resilient surface comprising a plurality of undercut-shaped microdepressions;

wherein the microstructured polymeric substrate comprises a plurality of undercut-shaped microprotrusions which are inverted replicas of the microdepressions.

6) A polymeric substrate formed by a process comprising:

contacting a polymeric material in a flowable state with a resilient surface, the resilient surface comprising a plurality of first microaberrations;

wherein a microstructured polymeric substrate is formed, the microstructured polymeric substrate comprising a plurality of second microaberrations which are inverted replicas of the first microaberrations.

7) A polymeric substrate of unitary construction comprising a plurality of undercut-shaped solid microprotrusions.

8) The polymeric substrate of claim 7 further comprising a plurality of projecting elements comprising an outer surface, the outer surface comprising a plurality of the microprotrusions.

9) A polymeric substrate comprising a plurality of projecting elements comprising an outer surface which comprises sidewalls, said sidewalls comprising a plurality of solid microprotrusions, said microprotrusions having a width of about 10μm to about 400μm and a height of about 10μm to about 400μm.

10) The polymeric substrate of claim 9 wherein the projecting elements comprise a sidewall having a draft of no more than about 30°.

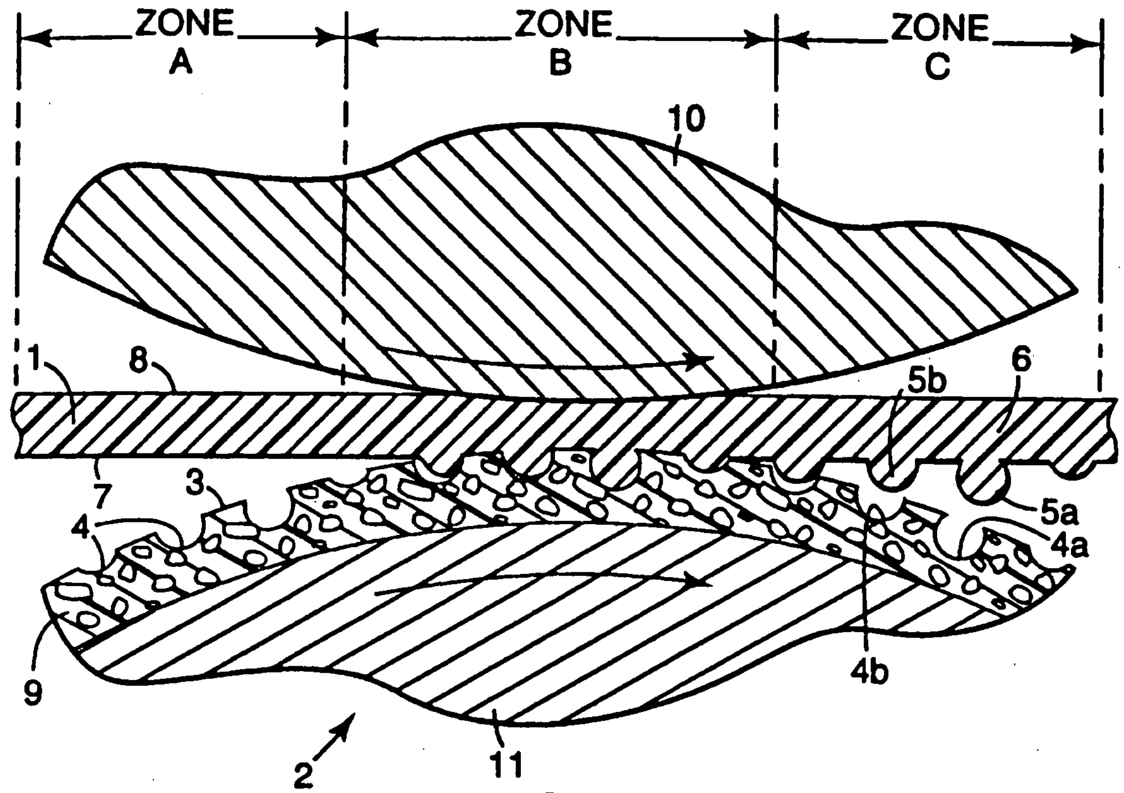
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FIG. 1

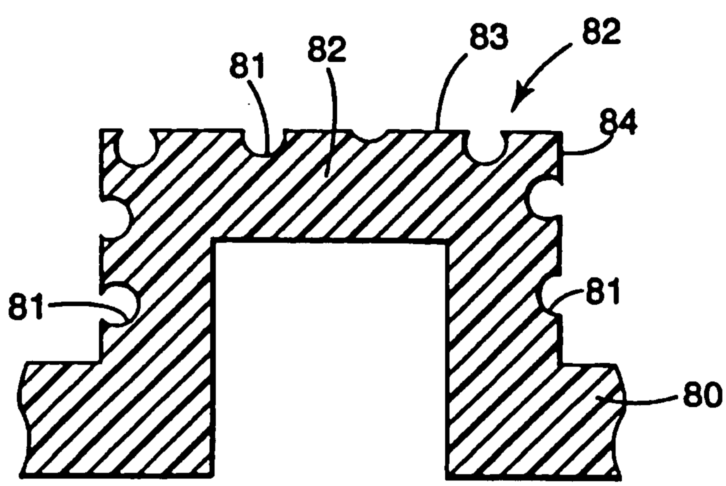
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FIG. 5

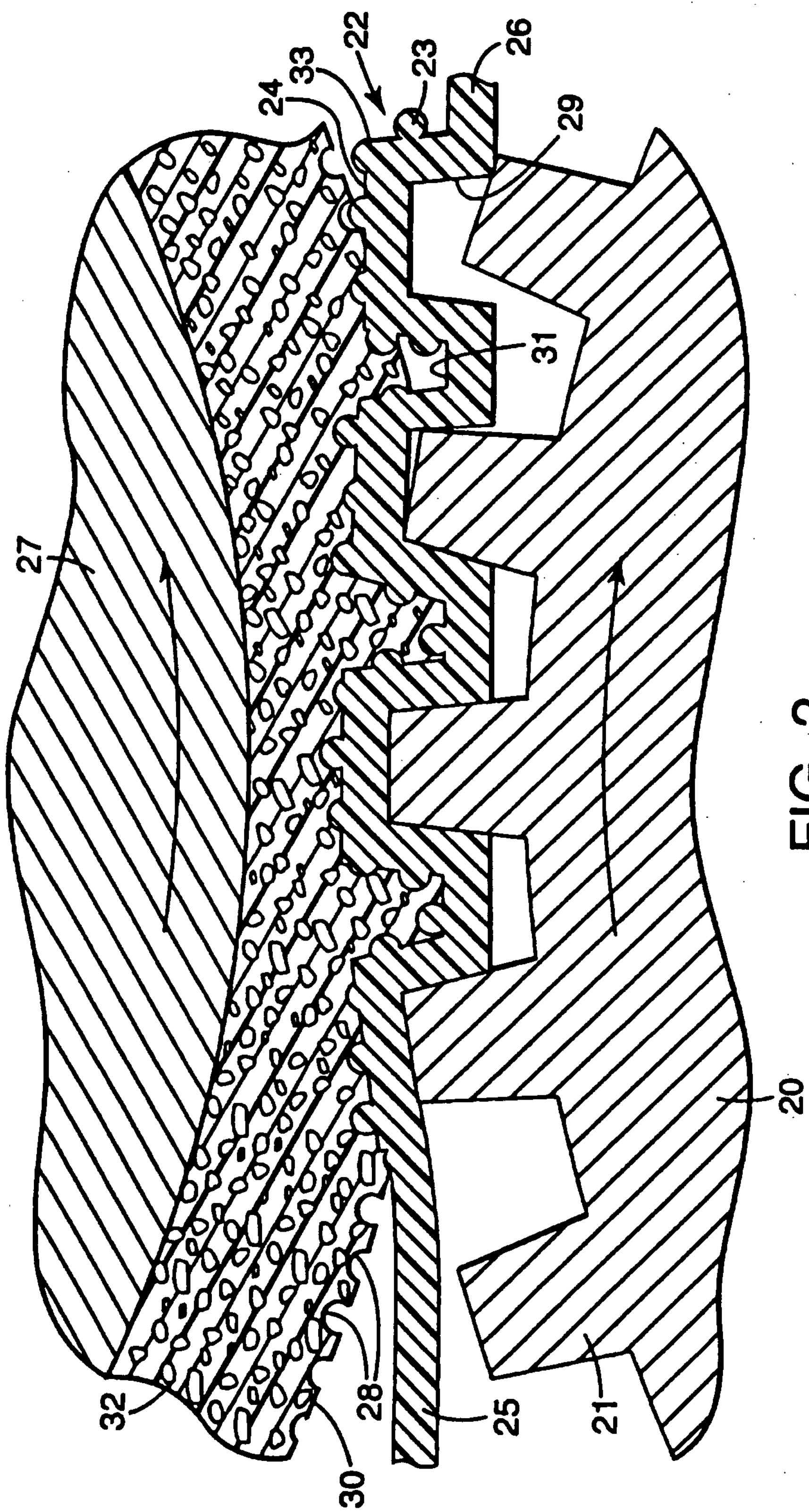


FIG. 2

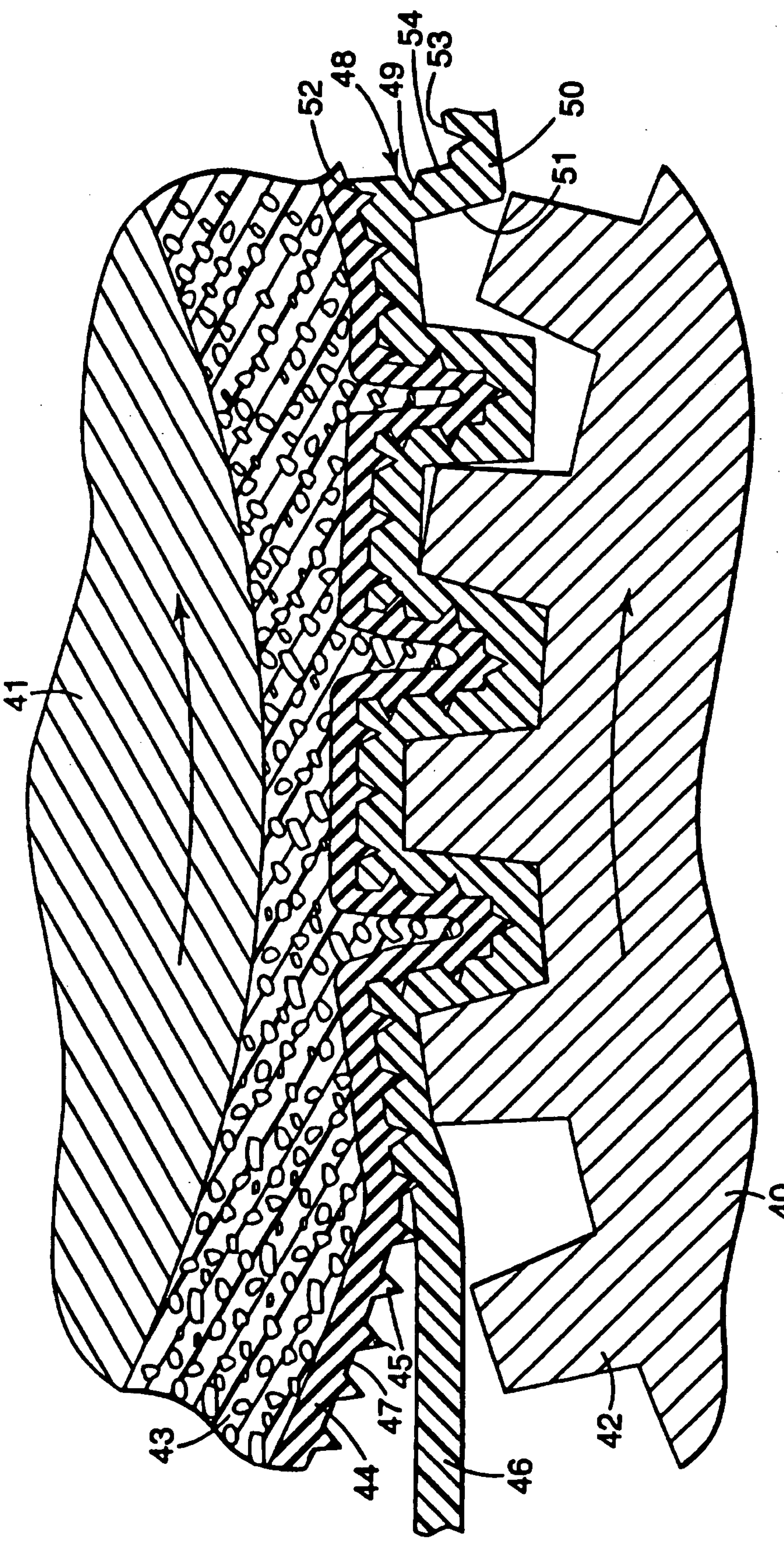


FIG. 3

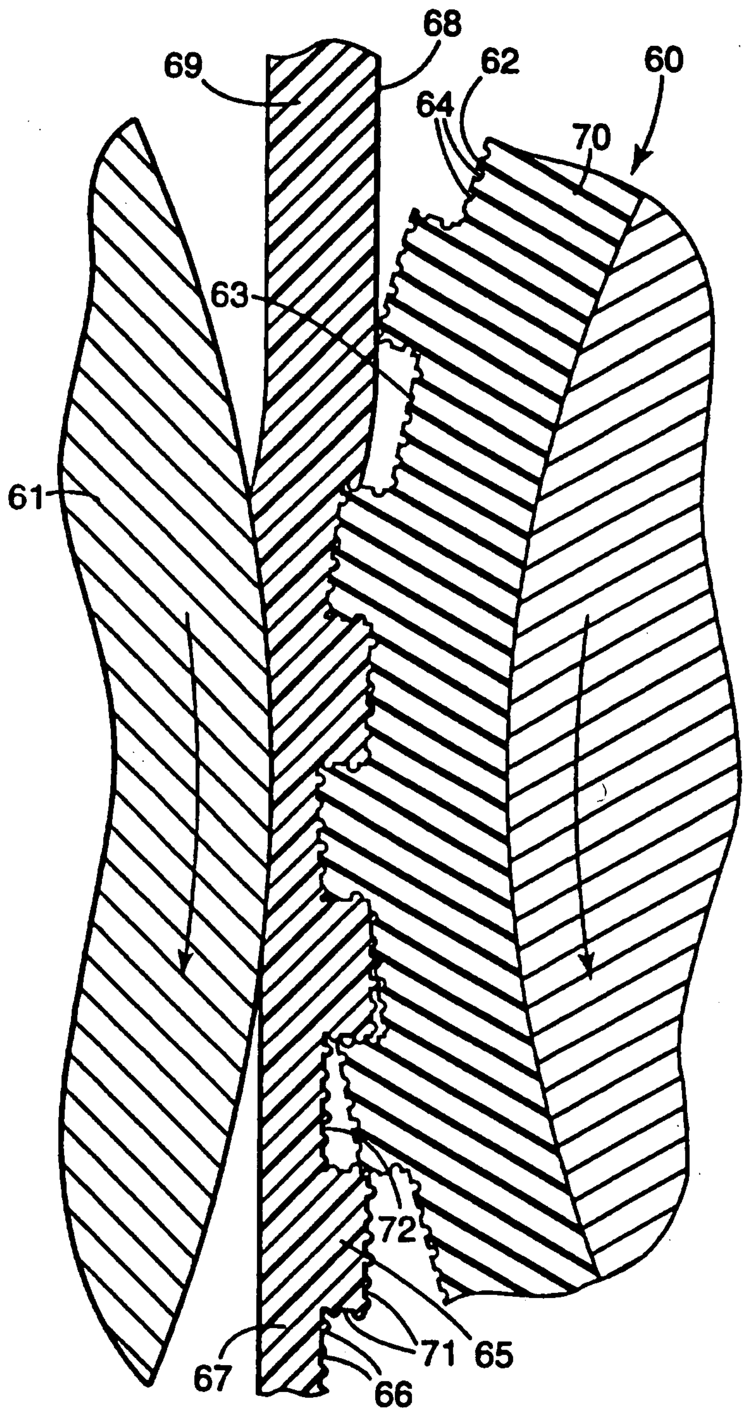


FIG. 4

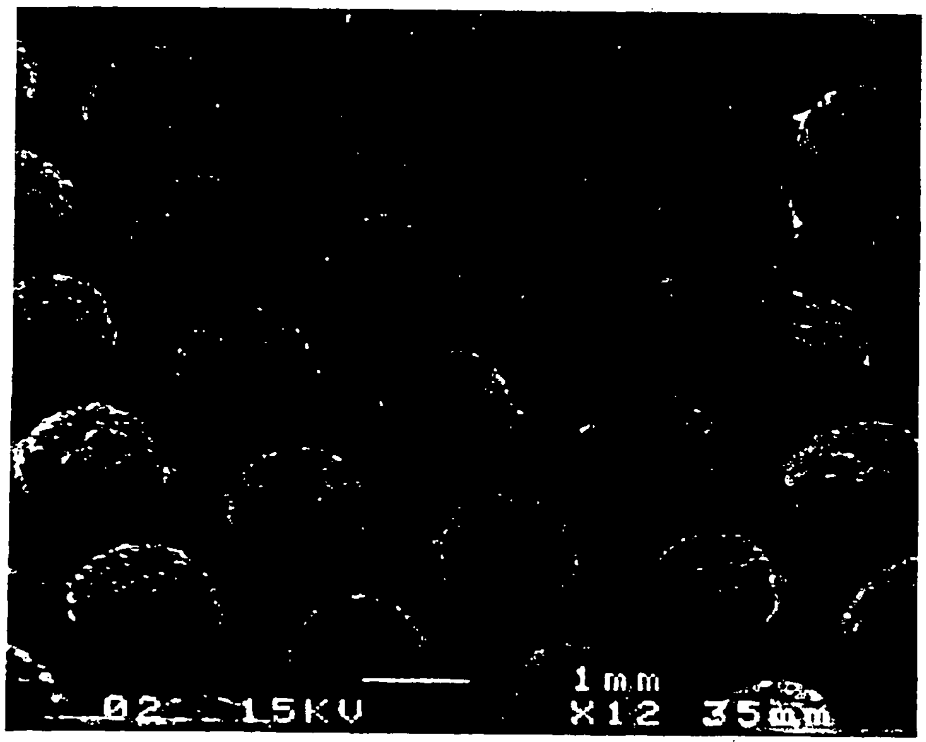


FIG.6

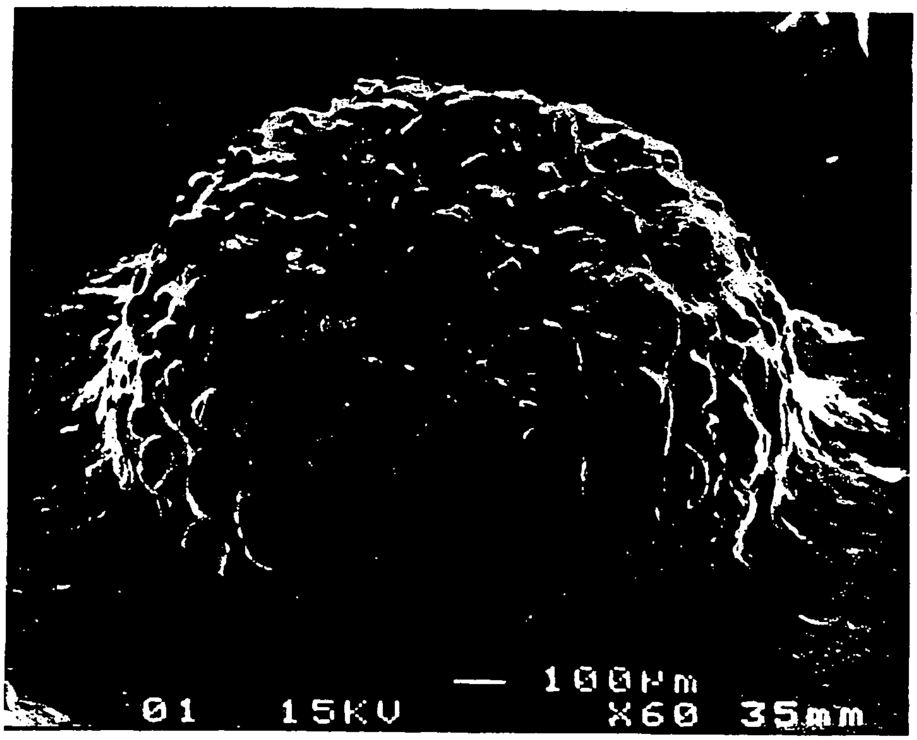


FIG.7

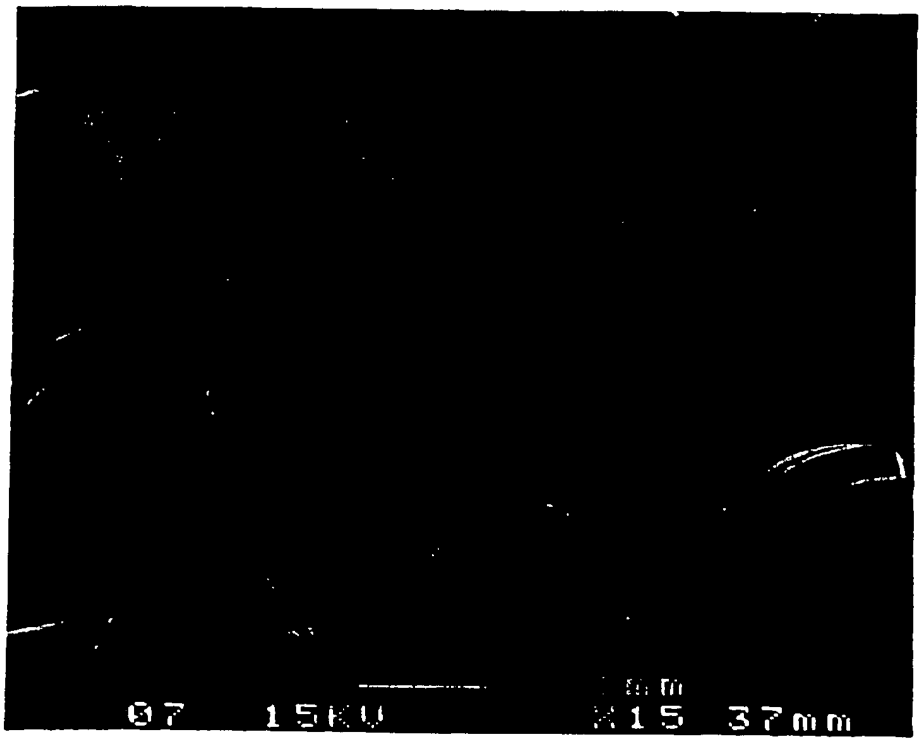


FIG.8

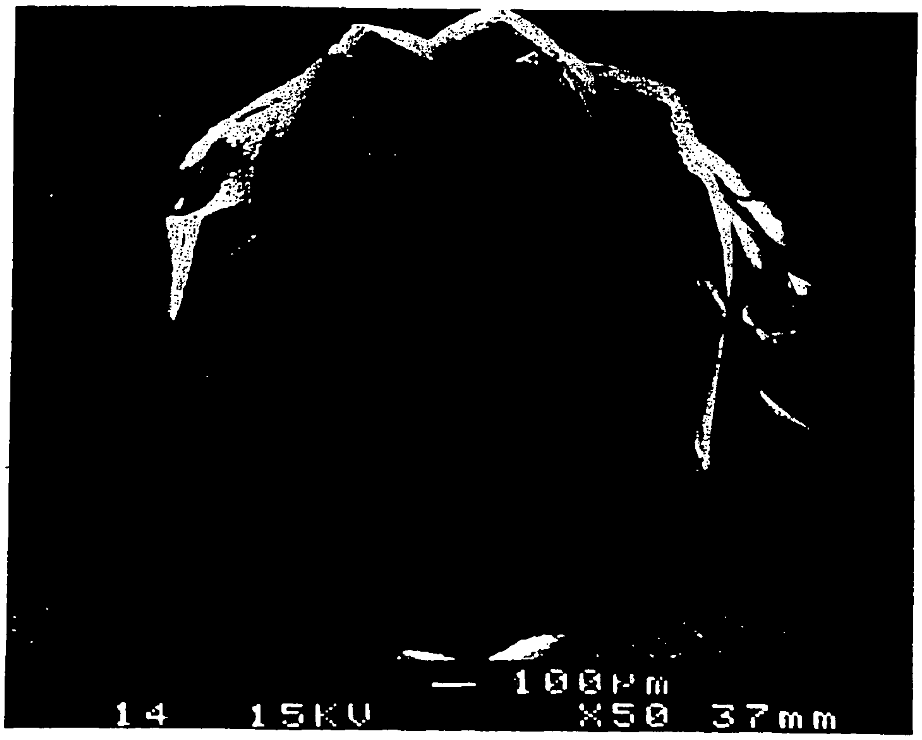


FIG.9

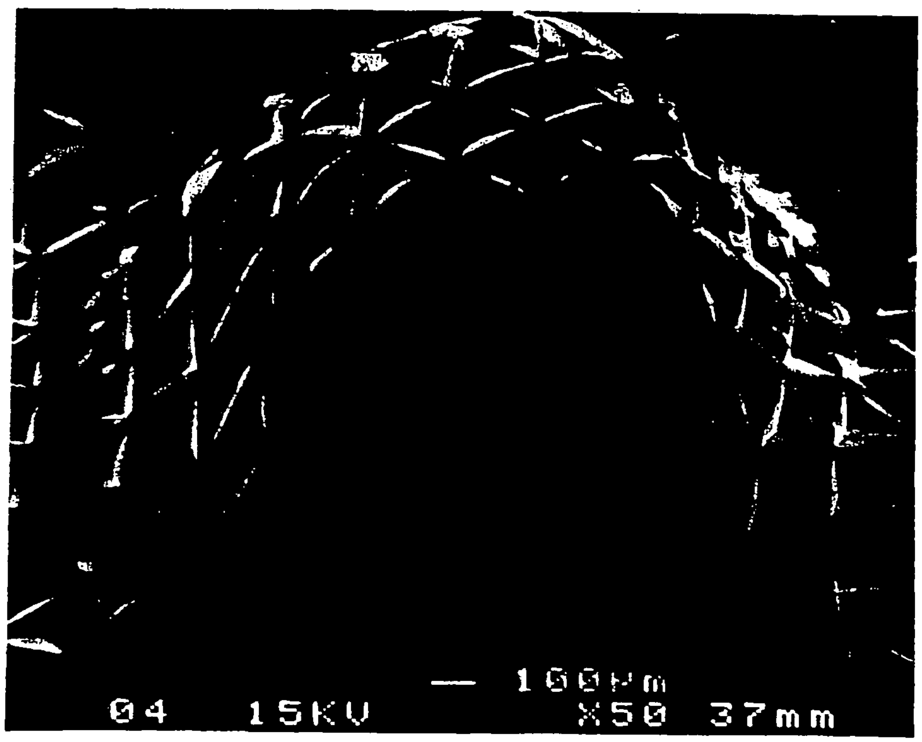


FIG.10

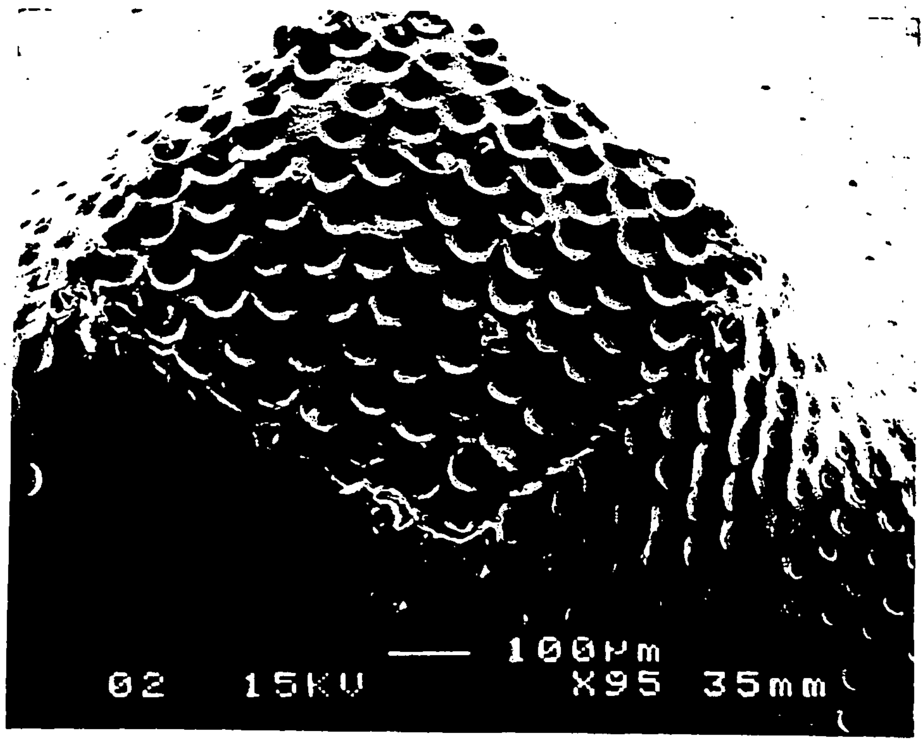


FIG.11

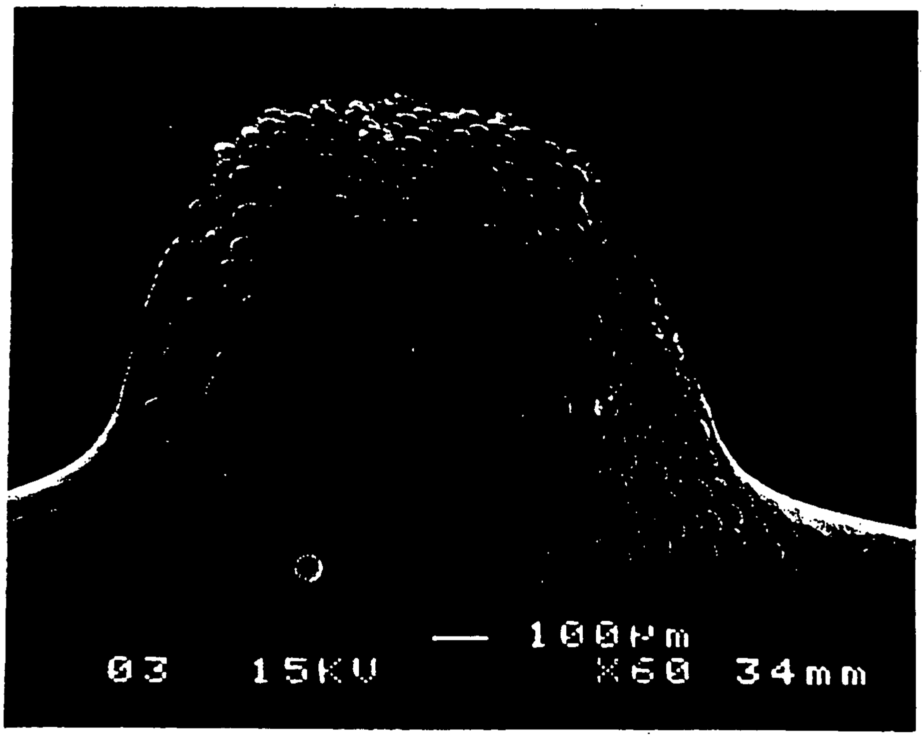


FIG.12

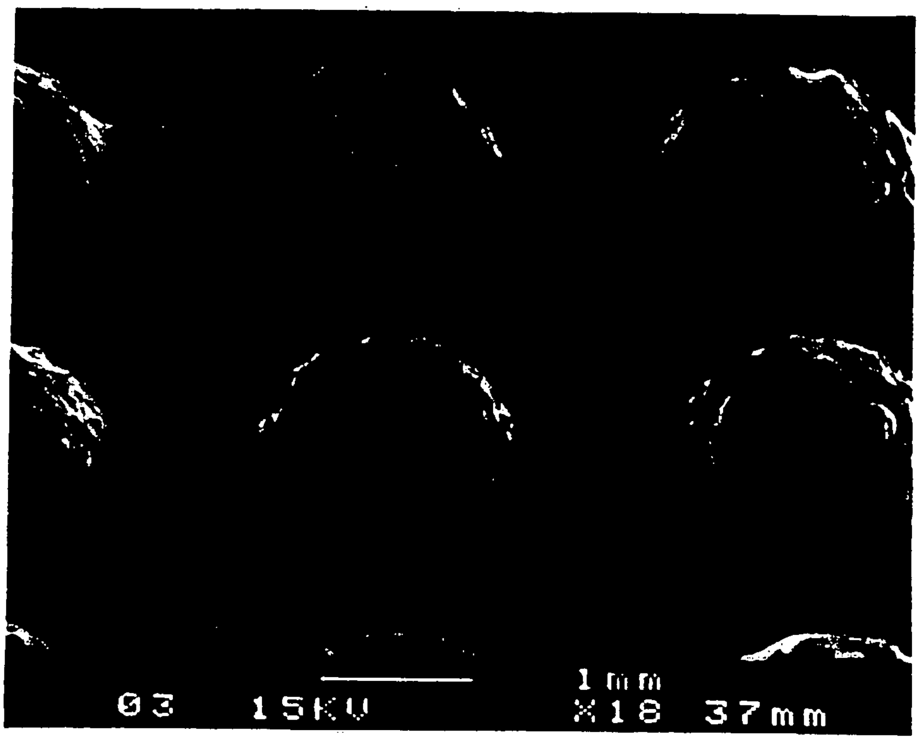


FIG.13

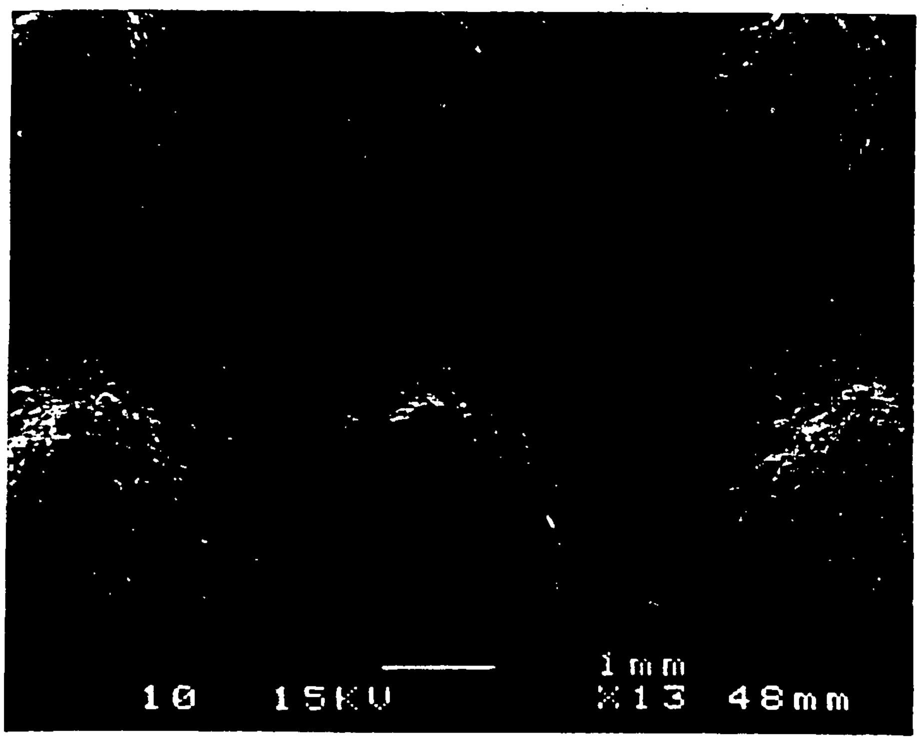


FIG.14

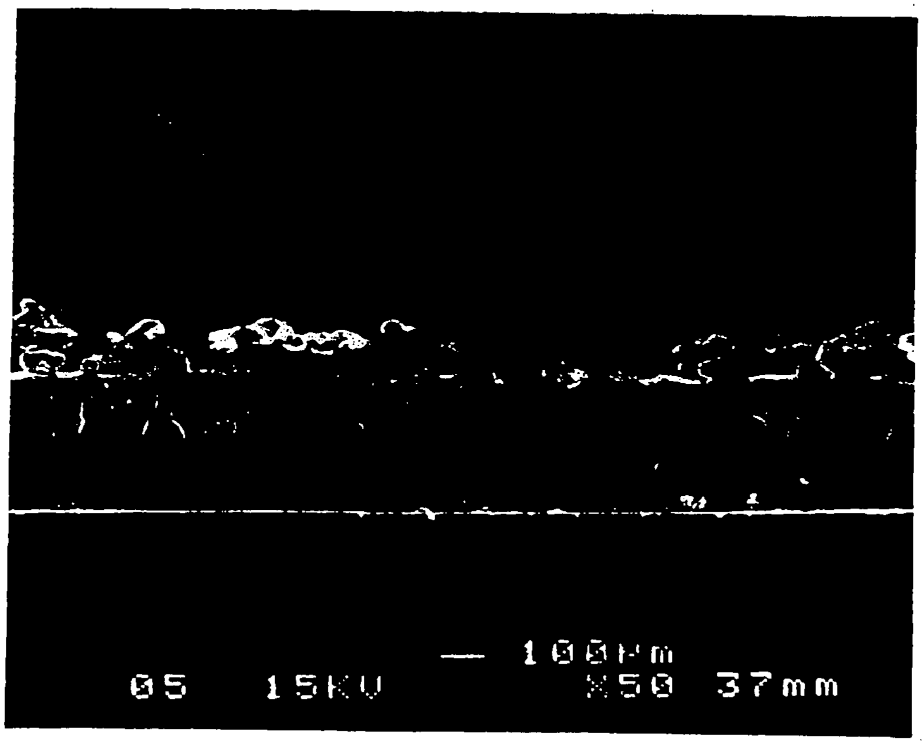
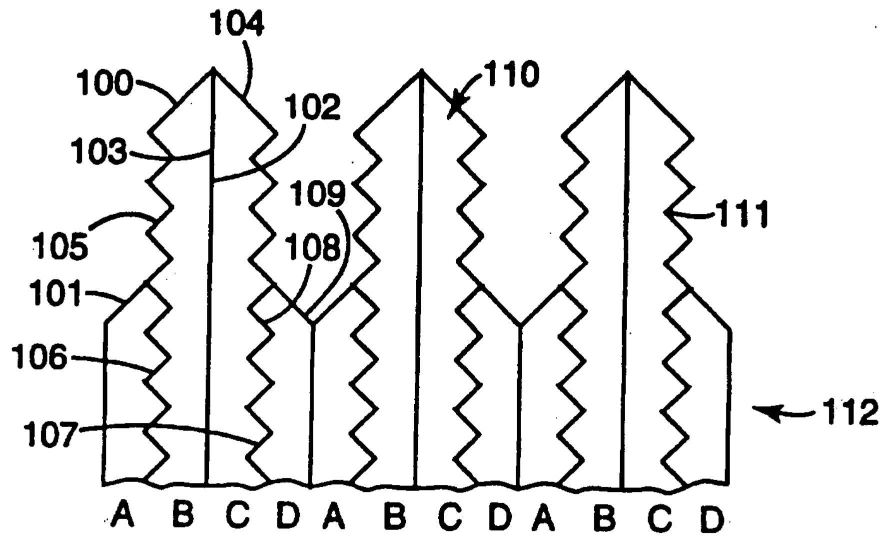


FIG.15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A B C D A B C D A B C D

FIG. 16

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/14825

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C59/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 211 743 (KOS JACOB J ET AL) 8 July 1980 see the whole document ---	1-3,6,9,10
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
23 December 1996	15.01.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Labeeuw, R

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C.(Continuation) DOCUMENTS [illegible]IDERED TO BE RELEVANT

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X	DE,A,26 12 767 (ARMSTRONG CORK CO) 18 November 1976 see the whole document ---	9,10
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A	FR,A,2 105 279 (ERNEST SCRAGG & SONS) 28 April 1972 see page 3, line 13 - line 25 -----	5,7

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